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Use of Saponins as an Effective Surface Modifier in Cellulose Nanocomposites

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The present paper deals with the extraction of saponins from the pericarp of Sapindus mukorossi *to use as compatibilizer in nanocomposites. The nanofibrils extracted from banana fibres are utilized as reinforcement of nanocomposite. These nanofibers were treated with Saponin, GPS (3-Glycidoxypropyltrimethoxysilane) and APS (3-Aminopropyltriethoxysilane) to compare the effectiveness of surface treatment. The effectiveness of surface modification was reflected on the increase in mechanical (tensile test, flexural modulus, impact test) properties and decrease in the RMS (Roughness Measurement System) roughness investigation by SFM (Scanning force microscopy) analysis.*

Keywords Banana nanofibres; nanocellulose; nanocomposites; saponins; surface modification

Introduction

Miniaturized materials used for manufacturing are a trend in technology development. Coupled to this there is growing interest in the development of bio-based products that can reduce dependence on fossil fuel [1]. Scientists and engineers have therefore begun focusing their research on the production of nanocomposites from renewable resources.

Conceptually nanocomposites refer to multiphase materials in which at least one of the constituent phases has one dimension less than 100 nm. Similar to traditional microcomposites, nanocomposites use a matrix in which the nano-sized reinforcement elements are dispersed, separated chemically by an interface adhesion. The reinforcement is currently considered a nanoparticle. This particular feature gives nanocomposites unique and outstanding properties which are different from those found in conventional composites [2]. These nanomaterials are referred to in the literature as nanofillers, nanoparticles or nanoreinforcements [3].

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In recent years, the use of cellulose nanofibres as reinforcing agents in biodegradable polymer systems has attracted a great deal of attention. As one of the most important subgroups of polysaccharides, cellulose is a ubiquitous and abundant structural polymer found in plants and animals, even in primitive organisms such as bacteria, fungi, algae and amoebas [4]. Nanocellulose has attracted a great deal of interest in the nanocomposites field due to its appealing intrinsic properties, such as its nanoscale dimensions, high surface area, unique morphology, low density and mechanical strength, as well as the fact that it is readily available, renewable and biodegradable [5].

It is well known that the macroscopic properties of a composite material reinforced with nanometric fillers are determined by various factors, such as its composition, the characteristics of each component, the geometry of the filler, the filler dispersion, the filler/filler and filler/matrix interactions and, in some cases, the modification of the characteristics of the matrix itself [6]. That is to say, the surface characteristics play a vital role in the functioning of a biomaterial. The key physical properties of a biomaterial can be retained, while only the outermost surface is modified to tailor the bio-interactions. Hence, if the surface is properly modified, the mechanical properties and functionality of the device will remain unaffected, but the tissue interface-related biocompatibility can be improved [7].

Surface modification techniques have become a key method for designing materials to produce specific biological and chemical interactions. Modification of surface properties by altering the surface functionality or by thin film deposition allow us to create and optimize surfaces with chemical and physical properties that are suitable for biological evaluation, as well as for many other applications such as the facilitation of particular cell/protein responses to a surface. By introducing the type and the amount of chemical functionality required, a convenient means of controlling and achieving the desired response can be obtained. Since the development of suitable materials requires a thorough understanding of the structure and chemistry of the solid/environment interface, it is essential to combine surface modification with surface analysis. The properties that can be altered include: hydrophilicity, hydrophobicity, the ability to form covalent bonds and the formation of protective barriers. Alteration of these properties will allow us to improve or control, among other things, adhesion, bonding of reactive components and cell response.

With the growing interest in the development of bio-based products in mind, we attempted to develop an effective natural surface modifier extracted from *Sapindus mukorossi* for nanofibre modification. This has not been attempted before. The compatibiliser that has recently been used for modification (methylenediphenyl diisocyanate (MDI)) appears to be toxic, and causes the environmentally friendly cellulose nanofibres to become non-biodegradable. The natural compatibiliser that we developed retains the biodegradability, sustainability and non-toxicity of the nanocellulose, which can be used for completely green nanocomposites.

Saponins are widely distributed secondary plant metabolites found among almost 100 plant families [8,9]. Saponins are a class of natural products: they are surface-active sterol or triterpene glycosides. Triterpenoid saponins consist of a triterpenoid aglycone composed of a C30 pentacyclic structure. Triterpenic saponins may be monodesmosidic or bidesmosidic, based on the attachment of sugar in either C-3-OH or C-28-COOH or both. Saponins are biological detergents because of the glycolysation of the hydrophobic aglycone. When agitated in water, they produce copious foam.

Saponins from *Sapindus mukorossi* (Sapindaceae) are used as a level-dyeing agent in dye baths, as emulsifier in the preparation of insecticides, and as a foam stabilizer in the manufacture of soapless shampoos, germicides and deodorizing agents. *S. mukorossi*, better known as "soapnuts", generally grow in the tropical and subtropical regions of Asia.

It has been reported that *S. mukorossi* possesses efficient natural surfactants and has been used as a commercial ingredient in shampoo and cosmetic cleansers [10]. In addition, some pharmacological effects, including anthelmintic, antidermatophytic [11], anti-inflammatory [12], antimicrobial [13], antitussive [11], cytotoxic [14], haemolytic [15] and molluscicida [16] activities, have been found in the plant. Regarding the principal constituents of these plants, various triterpenoid saponins containing dammarane-type [17,18], hederagenin-type [11,19], tirucallane-type [8,9], as well as sesquiterpene oligoglycosides [10,11], have been isolated from the fruit, gall, pericarp, root and stem.

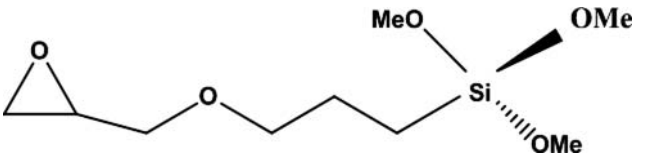
The aim of the present study was to examine the effect of surface modification of cellulose nanofibres from the banana pseudo-stem using natural surfactant and to investigate the reinforcing effect of surface-modified nanosized cellulose fibrils in the polypropylene matrix and compare the properties with chemical modifiers. Our group was the first to use saponin as a surface modifier for nanofibres.

Experimental

Materials

The materials used for the study included banana fibres (collected from Marthandom, Tamil Nadu, India), NaOH (commercial grade), acetic acid (commercial grade), sodium hypochlorite (commercial grade), oxalic acid (commercial grade). The equipment included a mechanical stirrer of type RQ-1.27 A; 8,000 r/min was used. Polypropylene (PP-Moplen RP 220 N) was used as the matrix.

The chemicals used for fibre surface modifications were 3-Glycidoxypropyl-trimethoxysilane (reagent grade), 3-Aminopropyltriethoxysilane (reagent grade) and saponins containing triterpene or steroidal aglycones-sapogenins derived from the soapnut (*S. mukurossi*). The structure of the coupling agents used is given in Schemes 1 to 3.

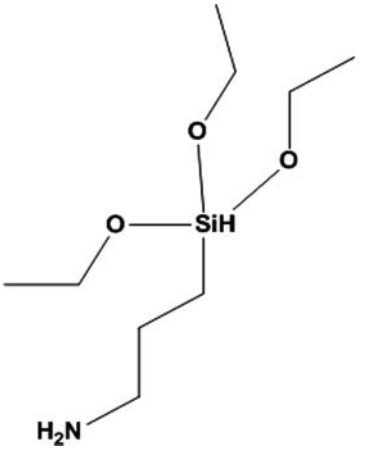


Scheme 1. Structure of 3-glycidoxypropyl trimethoxysilane.

Fibre Surface Modifications

Silane Treatment. For the surface treatment of the cellulose fibres, 5 wt% 3-Aminopropyltriethoxysilane (APS) and 3-Glycidoxypropyltrimethoxysilane (GPS) (weight percentage compared with the fibre) was dissolved for hydrolysis in a water-ethanol mixture (40:60 w/w) [1–5]. The pH of the solution was adjusted to 4 with acetic acid and stirred continuously for 1 h. Next, the fibres were soaked in the solution for 3 h. The fibres were then allowed to drain off free-flowing water and kept in air for 1 day. Lastly, the fibres were oven dried at 80°C for 24 h.

Natural Surfactant Treatment. The soapnuts were obtained from the trees of *S. mukorrossi* which are widely distributed in the southern parts of India. The extracts from the soapnuts



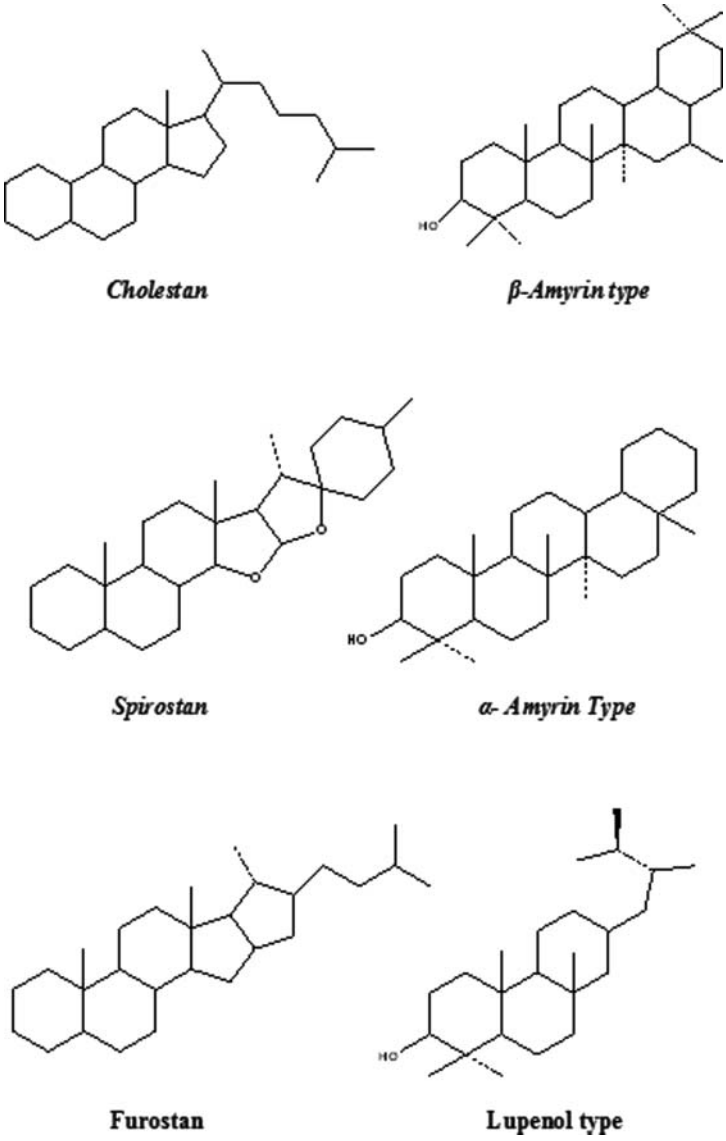
Scheme 2. Structure of 3-aminopropyl triethoxysilane.

were concentrated and the saponin was obtained by treatment with ammonium sulphate. The saponin was then washed with a solution of ammonium sulphate and dried. The cellulosic fibres were soaked in a water-saponin solution (10:90 w/w) for 3 days. The treated fibres were allowed to drain off free-flowing water and kept in air for 1 day. Lastly, they were oven dried at 80°C for 24 h.

Isolation of the Nanofibres. Banana fibres were chopped into uniform-sized pieces of approximately 10 cm. The fibres were treated with 2% NaOH (fibre-to-liquor ratio of 1:10) in an autoclave and kept under a pressure of 20 psi for a further period of 1 h. The pressure was released immediately and the fibres were removed from the autoclave and washed in water until they were alkali free. Free-flowing water was allowed to drain off the washed fibres. The steam-exploded fibres were bleached using a mixture of NaOH and acetic acid (27 g and 78.8 g respectively) and a mixture of 1:3 sodium hypochlorite solution. The bleaching was repeated six times. After bleaching, the fibres were thoroughly washed in distilled water and dried. The steam-exploded bleached fibres were treated with oxalic acid of 11% concentration in an autoclave until a pressure of 20 psi was reached. The pressure was released immediately. The autoclave was again set to reach 20 psi and the fibres were kept under that pressure for 15 min. The pressure was released and the process repeated eight times. The fibres were taken out and washed until washing no longer decolorized the $KMnO_4$ solution to ensure that the washed fibres were free from acid. The nanofibrils obtained were suspended in water and stirred continuously with a mechanical stirrer of type RQ-1.27 A, at 8,000 r/min for about 4 hours until the fibres were uniformly dispersed. The suspension was placed in an oven at 90°C until it was dry.

Processing of Polypropylene (Thermoplastic) Nanocomposites

Compounding and Granule Preparation. The banana microfibrils were initially weighed and bagged to determine the different composition of the fibres. The fibres were compounded with PP granules in a Brabender Plasticoder at a temperature of 150°C and a speed of 50 r/min. The compounded materials were then ground to prepare the granules.



Scheme 3. Basic sapogenin skeletons–steroidal (left column) and triterpene (right column).

Granules of the chemically treated nanofibrils with fibre loadings of 4, 8 and 12% were also prepared by this method.

Injection Moulding. The thermoplastic (PP) and the granules of cellulose nanofibres-reinforced biocomposites were injection moulded in an 85 ton BOY 22D injection milder at a processing temperature of 130°C. Injection-moulded standard ASTM specimens were obtained for mechanical and thermal testing.

Characterization

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

A Shimadzu IR- 470 infrared spectrophotometer was used to obtain spectra for the fibers after each chemical treatment. KBr disk method was followed in taking IR spectra. Fibers were ground and mixed with KBr (sample/KBr ratio, 1/99) to prepare pastilles. FTIR spectra was recorded in a spectral range of 4,000-400 cm^{-1} with a resolution of 4 cm^{-1} with a total of 20 scans for each sample.

Morphological Analysis

Scanning Force Microscopy (SFM) Analysis. Cellulose microfibrils were observed using atomic force microscopy (NanoScope IVa, Multimode SPM–Veeco Inc. Santa Barbara, US), in tapping mode. Calibration was performed by scanning a calibration grid of precisely known dimensions. All scans were performed in air with commercial Si Nanoprobe SPM tips with a resonance frequency of about 300–330 kHz. A free amplitude (A_0) of about 20 nm and a set-point ratio (r_{sp}) between 0.4 and 0.6 were used. r_{sp} is the ratio between the set-point amplitude (A_{sp}) and A_0. Image processing, including flattening, was carried out. Height and phase images were obtained simultaneously in tapping mode at the fundamental resonance frequency of the cantilever with a scan rate of 0.5 line/s using a j-type scanner. The free oscillating amplitude was 3.0 V and the set-point amplitude was chosen individually for each sample. For each sample, images of at least five different fibres were scanned. Usually, two different areas of each fibre were investigated. Only one representative image per sample is shown. For SFM analysis of the cellulose nanofibril, samples for characterization were prepared by pipetting a 0.12 g/L aqueous whisker suspension, which was allowed to dry on a freshly cleaved mica surface at room temperature overnight. For bulk analysis of the nanocomposites, rectangular samples were cut and polished. The samples were then trimmed in a Leica Ultracut EM UC6 ultramicrotome in liquid nitrogen with freshly cleaved glass knives to obtain a rectangular block surface $50 \times 500\ \mu m^2$ in cross-section. For SFM analysis, the block surface should preferably be as large as possible. However, in order to minimize smearing of the outermost surface during cutting, a small block surface is believed to be advantageous. The final cutting was done with a diamond knife using a cutting speed of 0.4 mm/s to produce foils 50 nm thick.

Mechanical Testing. The static mechanical properties of the samples were investigated according to DIN EN 52, ASTM D790–97 and ISO 179. The mechanical properties of the composites were evaluated using tensile, flexural and impact tests.

Tensile Testing. All the samples for tensile testing were cut into dog-bone shape. The tensile tests were done to the point of tensile failure on a Zwick Z250 tensile testing machine according to DIN EN 52. Ten samples were tested and at least five replicate samples were presented as an average of the tested samples.

Flexural Modulus. All the flexural testing samples were cut into rectangular shape. Three-point bending tests were carried out on the samples according to DIN ISO 178 with ASTM D790–97 standard. The support span was 43 mm and the cross-head speed was 1.3 mm/min. Ten samples were tested and at least five replicate samples were presented as an average of the tested samples.

Table 1. FTIR spectral data (KBr, cm^{-1})

Wave number cm^{-1}	Assignment
3400	–OH stretching
2967-2877	Aliphatic C–H stretching
1744	C = O stretching stretching (for ester)
1629	C = C stretching
1450	C–H bending ($–CH_2$)
1375	C–H bending ($–CH_3$)
1240	C-O-C Vibrations in Esters
1041	C–O stretching

Impact Testing. All the impact testing samples were cut into rectangular shape and notched. Charpy impact strength (unnotched) was measured in a WinPEN CEAST (SpA, Italy), according to ISO 179. The samples were measured at an impact energy of 1 J and an impact velocity of 2.9 m/s with dissipation energy of 0.018 J. Ten samples were tested and at least five replicate samples were presented as an average of the tested samples.

Results and Discussion

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The presence of various functional groups forming the hydrophobic and hydrophilic parts of soapnut, and which contribute to it being an effective foam stabilizer, were confirmed through FTIR. Table 1 gives the assignment of IR absorption peaks of the samples analysed. The presence of hydroxyl groups was indicated by the broad absorbance peak centering around 3400 to 3500 cm^{-1} in FTIR spectra (Fig. 1). The peak at 2967–2877 cm^{-1} is due to aliphatic saturated C−H stretching vibration in hemicellulose and cellulose. FTIR spectra of soapnut also showed absorbance peaks at 1635 and 1049 cm^{-1} suggesting the presence of acids and carbohydrates, respectively. The FTIR spectra of the cellulose nanofibre treated and untreated with saponin showed a characteristic strong carbonyl absorption peak at 1744 cm^{-1} indicates the presence of C=O group. The peak at 1621cm^{-1} is due to C=C vibration and a peak at approximately 1450 and 1375 cm^{-1} shows C−H bending ($-CH_2$) and C−H bending ($-CH_3$) respectively. An ester peak at 1240 cm^{-1} indicates the presence of C−O−C. The FTIR spectrum corresponding to saponin treated cellulose nanofibres is quite similar to that of the pure cellulose nanofibers.

Surface-Modified Cellulose-PP Composites

Figures 2–4 and 5 show the 3D tapping mode SFM images of pure, GPS-, saponin- and APS-treated nanocellulose-reinforced PP composites. The SFM analysis shows that surface modification of the nanocellulose causes a decrease in the surface roughness of the prepared composites. The hydrophobicity of the fibres produced causes them to be very compatible with the matrix, which causes diminishing of the peak valley structures in the treated composites. Maximum surface roughness is observed in composites reinforced with APS-treated fibres, and minimum surface roughness in composites produced with GPS-treated fibres. The RMS roughness of the composite samples treated with GPS, saponin and APS

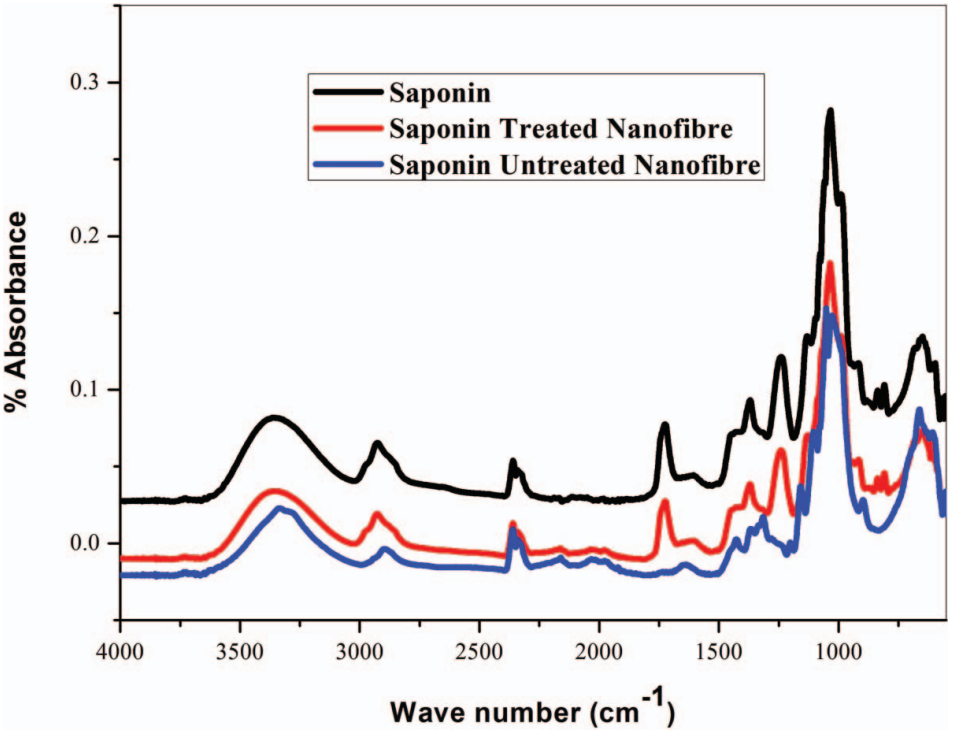


Figure 1. Three-dimensional tapping mode SFM images of pure PP composite.

was calculated to be 2.13 nm, 5.28 nm and 12.55 nm respectively, showing an increase in the fibre-matrix adhesion.

Effect of Fibre Surface Modifications on the Mechanical Performance of the Composites

Figures 6 and 7 shows the variation in tensile strength and modulus of the different modified fibre composites, respectively. It can be seen that the tensile strength and modulus of the modified fibre composites is greater than that of the untreated fibre, which is due mainly to the high fibre-matrix interaction occurring during the treatment process. The tensile strength was higher for the GPS-treated fibre-reinforced composites and lower for the APS-treated composites. A similar trend was observed for the flexural strength and modulus of the modified fibre composites. The minimum modulus was observed for the APS-treated composites and the maximum for the GPS-treated nanofibril composites. The flexural strength of the modified composites also show a similar trend. A sharper increase in the flexural properties of the treated composites was observed than in the untreated composite (Figs. 8 and 9). The surface modification caused the cellulose fibres to become hydrophobic, which increases the interaction with highly non-polar polypropylene resin. Chemical modifications may decrease the hydrophilicity of the cellulosic fibre, thereby increasing the interfacial adhesion, which is expected to improve the mechanical properties of the modified fibre-reinforced nanocomposites. The fibre surface modification causes the cellulose fibre to become hydrophobic due to the attachment of bulky chemical groups

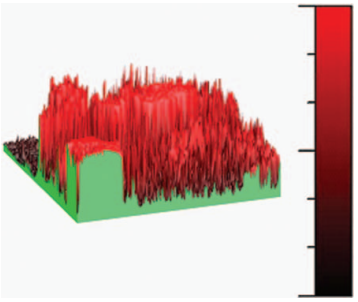


Figure 2. Three-dimensional tapping mode SFM images of GPS-treated, nanofibre-loaded PP composite.

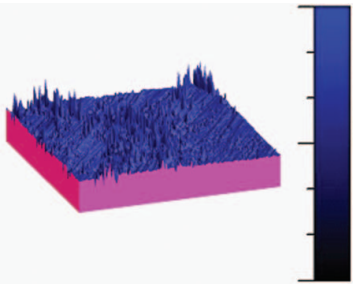


Figure 3. Three-dimensional tapping mode SFM images of saponin-treated, nanofibre-loaded PP composite.

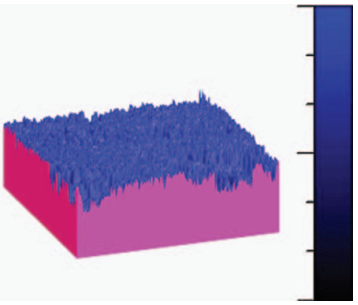


Figure 4. Three-dimensional tapping mode SFM images of APS-treated, nanofibre-loaded PP composite.

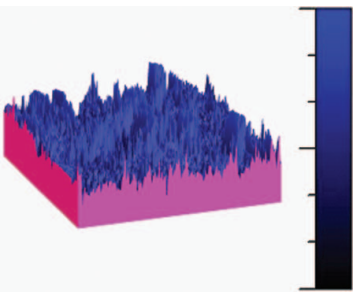


Figure 5. Variation of tensile strength in different treated cellulose–PP composites.

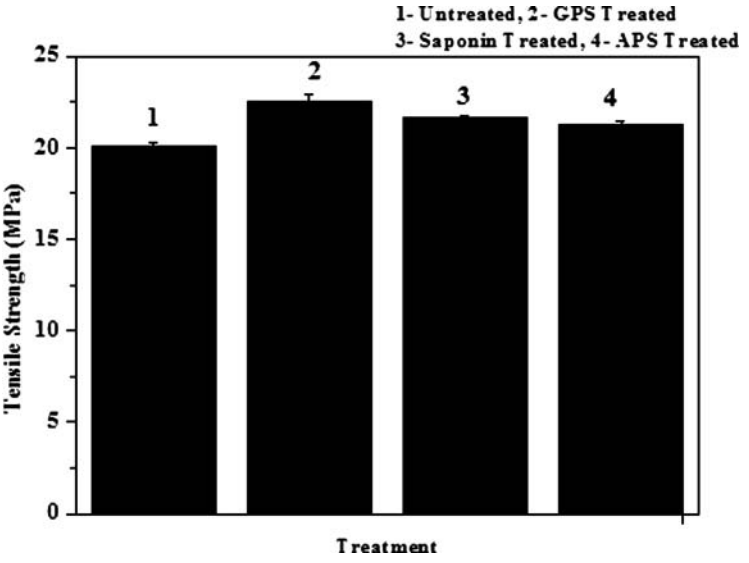


Figure 6. Variation of Tensile Strength with treated cellulose–PP composite.

on the fibre surface, which facilitates smoother interaction of the fibre with the matrix. In general, the use of coupling agents, such as natural surfactants and silanes, significantly increases the positive mechanical properties of the PP nanocomposites, since the matrix is hydrophobic in nature as discussed below in the section on the mechanical performance of nanofibres-reinforced composites.

The impact properties of treated fibre composite (Fig. 10) show maximum strength for APS-treated samples and minimum strength for GPS-treated samples. The impact parameter of treated fibre composites was found to be higher than that of untreated composites.

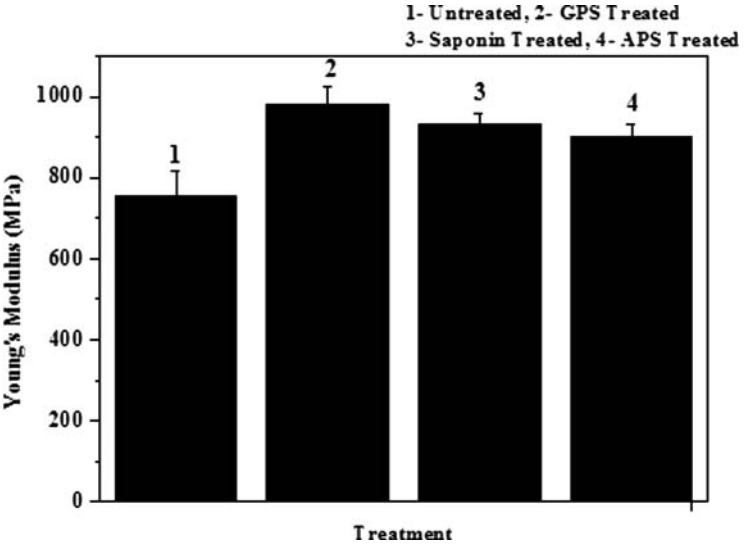


Figure 7. Variation in Young's Modulus with different treated cellulose–PP composites.

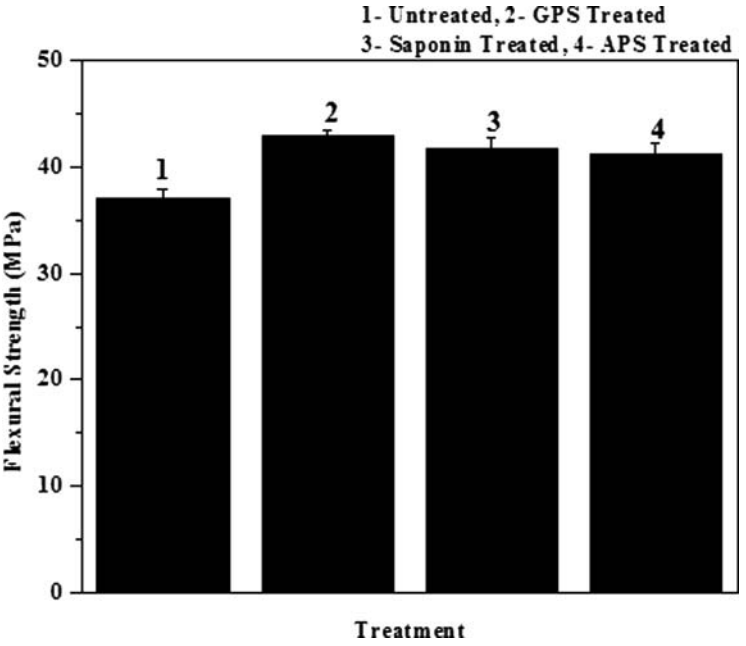


Figure 8. Variation of flexural strength with different treated cellulose–PP composite.

Impact strengths of treated nanocellulose fiber composites are compared with untreated as shown in Fig. 10. The impact performance of fiber-reinforced composites depends on many factors, including the nature of the constituent, fibre/matrix interface, the construction and geometry of the composite and test conditions. The impact failure of a composite

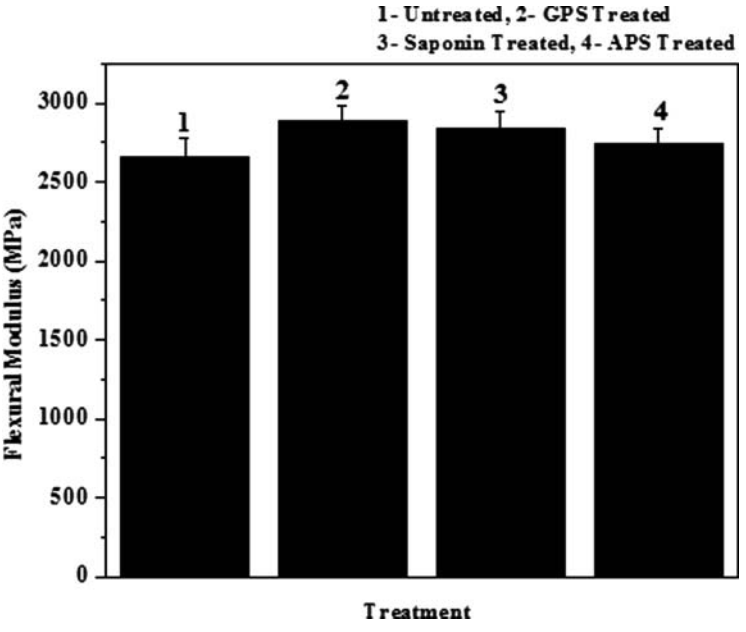


Figure 9. Variation of Flexural Modulus with different treated cellulose–PP composite.

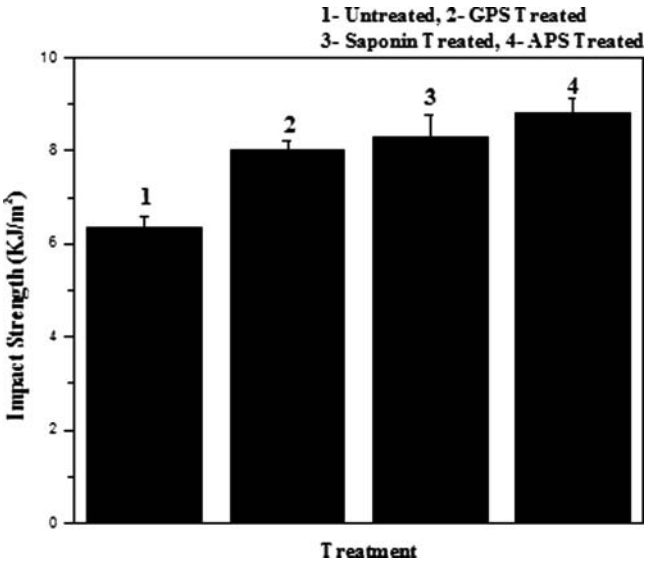


Figure 10. Variation of impact strength with different treated cellulose–PP composite.

occurs by factors like matrix fracture, fiber/matrix debonding and fibre pullout. The impact strength is observed to be increased evidently in the order untreated, GPS, saponin and APS treatment. The increase in the impact property of the surface modified nanofiber composite can be justified as follows. The fibre modification leads to tincreased hydrophobicity of the cellulose fibres which in turn increases the fibre-matrix adhesion in the hydrophobic polymeric matrices, thus enhancing the reduced matrix fracture of these nanocomposites. The impact strength was found to be lowest for GPS treated nanofibre reinforced composites and almost medium for saponin and observed to be high for APS treated fibril composites. Thus, we can observe that all the fibre surface modifications add positively to the impact properties of the nanocomposites than the untreated fibril composite which is also supported by SFM analysis of the developed composites.

Conclusion

We found that saponin modification improved various properties of the nanocellulose nanofibres and their composites. The compatibility of the nanocellulose appeared to be significantly increased by the utilization of natural surfactant. The comparative study with chemical modifiers proved the effectiveness of the natural modifier, which was observed to be as effective as chemical modifiers. Due to the increase in the hydrophobic nature of cellulose nanofibres resulting from saponin treatment, there was a reduced decrease in surface roughness of the saponin-modified PP nanocomposites. The sharp increase in the mechanical properties of the nanocellulose-PP composites was also found to be promising for the use of saponin as an efficient nanocellulose surface modifier in a hydrophobic matrix such as polypropylene.

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